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Process for cleaning articles

DKS 41

This invention relates to a process for cleaning articles and materials of metal, glass, ceramics, plastics, or composites thereof or of textiles.

Cleaning processes in which a vapor produced by heating of an active cleaning liquid is brought into contact with articles to be cleaned are employed in the cleaning of a very wide variety of articles, such as metal articles, industrially manufactured articles such as circuit boards, articles of clothing, etc, to remove undesirable foreign substances such as fats, lapping and polishing pastes, soldering pastes, adhesives, mixtures of inorganic (e.g., saline) fouling substances and organic fouling substances (e.g., ones consisting of fatty residues), etc. Until recently chlorinated hydrocarbons were typically used for such cleaning tasks. But now, because of their inadequate environmental compatibility, and especially because of their ozone destruction potential, their carcinogenicity, and their toxic effect, they have been banned or use of them is allowed only under very strictly defined conditions. One advantage of using chlorinated hydrocarbons was that such substances have no flash point. Because of the disadvantages indicated they have been replaced by other hydrocarbons or solvents such as polypropyleneglycol ether, alcohols, acetone, and the like. The latter have flash points in the range of normally occurring temperatures and are consequently ignition hazardous. They also present another disadvantage in that they hardly remove pigment fouling or fouling with ionic salts, since these solvents are very inefficient in dissolving pigments or salts because of the ionic nature of the latter.

The object of the invention was to develop a generic cleaning process so that a good cleaning effect may be achieved in an environmentally compatible manner.

Another object of the invention was to prepare a new cleaning process whereby mixtures of inorganic and organic fouling may be eliminated simultaneously in an efficient manner. An additional object of the invention was represented by preparation of a process for cleaning metal articles and materials which is not as harsh in the results of its operation as are state-of-the-art processes.

The objects referred to above are attained by a process having the features specified in Claim 1 of the patent. Advantageous developments of the process claimed for the invention are presented in Claims 2 to 19.

Azeotropic preparations as claimed for the invention which are usable as active cleaning liquids yield the advantage above all that, because of the aqueous component, their liquid phase efficiently dissolves pigment fouling and fouling with ionic components such as salts, if the azeotropic preparation used as active cleaning liquid comes in contact with the articles. The molecules containing lipophilic groups of at least one additional component, which is preferably also a liquid under ambient conditions or at low treatment temperatures, ensure that the azeotropic preparation will possess efficient lipolytic capability.

If the azeotropic preparation used as active cleaning liquid is heated, because of its azeotropic nature (for a definition of "azeotrope" see Römpps Chemie Lexikon [Römp's Chemical Dictionary], 9th Edition (1989), page 323) both water and the other component(s) pass(es) into the vapor phase in a composition corresponding to that of the specific azeotrope. When the vapor of the azeotropic preparation comes into contact with the articles to be cleaned, reliable cleaning and "rinsing" from the articles to be

cleaned of the fouling substance removed by the cleaning process is effected.

It is particularly advantageous that the vapor, because of its high water content, is not combustible. Precautionary measures in this connection are superfluous in a device used for application of the process claimed for the invention. The flash point of the vapor, to the extent that such exists, is above the temperatures normally occurring in such a cleaning process, but at least above the boiling point of the liquid and preferably above about 200 °C. A flash point above 200 °C is especially preferable in that the precautionary measures to be taken in carrying out the cleaning process are less extensive than when active cleaning liquids with lower flash points are used. The azeotropic preparation present in at least one part of the process claimed for the invention may be condensed to the liquid phase either on the articles to be cleaned or by lowering of the temperature, so that costly measures to protect the atmosphere surrounding the device applied for carrying out the process such as are required in conventional processes may be dispensed with to the greatest possible extent.

Hence an additional advantage of the process claimed for the invention is represented by the fact that very little of the azeotropic preparation employed as active cleaning liquid is used because of recondensation of the liquid to the greatest extent possible. A closed loop may thus be created in which the azeotropic preparation used as active cleaning fluid need be replenished not at all or only in negligibly small amounts. An additional contribution to this result is made by the fact that the azeotropic preparation as claimed for the invention employed as active cleaning liquid may be free of surfactants, which are deposited on the filter surface during filtration of the active cleaning liquid in conventional processes for precipitation of fouling substances and require reinforcement in conventionally used solutions.

Surprisingly, the process claimed for the invention may also be used to remove complex kinds of fouling such as dried body fluids or other fouling substances occurring in everyday life as a result of precipitation in the form of rain or snow, etc, from articles to be cleaned.

The process claimed for the invention is not limited to closed systems. It may, for example, also be applied in the form of open jet steam cleaning.

In selection of the azeotropic preparations claimed for the invention used as active cleaning liquid or of the other component(s) which the preparations contain, with molecules having hydrophilic groups (e.g., -OH, -NH₂, -C-O-C-, C(=O)-C-, -C(=O)-O, etc) and lipophilic groups (e.g., CH₂ chains or C₁ to C₁₂, etc), emphasis is placed on the following criteria in addition to good cleaning power. The moisture content of the azeotrope consisting of water and another component or other components must be high enough so that there is no flash point, that is, so that the vapor is not combustible. The liquid and the vapor formed from it by heating must neither be toxic nor have an ozone destruction potential, nor may it trigger a water hazard if the preparation is inadvertently released into the environment. Water soluble components forming homogeneous azeotropes or water insoluble components forming heterogeneous azeotropes are suitable.

In a preferred embodiment the process claimed for the invention for cleaning articles comprises steps in which

- an azeotropic preparation is formed of water and at least one component with molecules having hydrophilic and lipophilic groups in a weight ratio (component(s) with hydrophilic and lipophilic groups) of water 0.05 to 99.5 : 99.95 to 0.05;

- the articles to be cleaned are brought at least once into contact with the azeotropic preparation and the liquid azeotropic preparation, including the foreign substances removed with it, is drained from the articles to be cleaned;

- residues of the azeotropic preparation on or in the articles to be cleaned are removed by evaporation; and

- the vapor of the azeotropic preparation is condensed and the azeotropic preparation recovered by condensation is used for a repeated cleaning step.

The foregoing corresponds to an especially preferred embodiment of the process claimed for the invention, one in which articles to be cleaned are brought at least once into contact with the vapor of the azeotropic preparation and the vapor of the azeotropic preparation is allowed to condense on the articles to be cleaned. For example, the articles to be cleaned may be brought into contact with the liquid azeotropic preparation only once or several times, for example, by immersion, spraying, sprinkling or the like, processes in the state-of-the-art already known for application of a liquid. The articles to be cleaned may subsequently be brought one or more times into contact with the azeotropic preparation in the form of the latter's vapor. The vapor of the azeotropic preparation condenses normally on the articles to be cleaned and carries with it residues of foreign substances from the articles to be cleaned as it drains. As an alternative, however, the process claimed for the invention may be applied by bringing articles to be cleaned immediately into contact with a vapor of the azeotropic preparation, at least once but preferably several times. In this instance as well the vapor condenses during contact on the articles to be cleaned and removes the fouling substances.

In an especially preferred embodiment of the process use is made of an azeotropic preparation of water and at least one component with molecules having hydrophilic and lipophilic groups, a preparation in which the weight ratio (of component(s) having hydrophilic and lipophilic groups) to water is in the range of 1.0 to 35.0 : 99.0 to 65.0, and even more to be preferred in the range of 4.0 to 15.0 : 96.0 to 85.0.

Corresponding to another preferred embodiment of the process claimed for the invention is use of an azeotropic preparation in the form of a mixture of water and at least one additional component with molecules having hydrophilic and lipophilic groups as active cleaning liquid, the additional component(s) and the water forming an azeotrope in the liquid-phase-to-vapor-phase transition and the azeotrope being an azeotrope with an immiscibility gap at a temperature ranging from 0 °C to the temperature of the phase liquid-phase-to-vapor-phase transition under normal pressure. Surprisingly, it has been found that azeotropes with immiscibility gaps possess particularly advantageous cleaning properties. Particular preference is to be given to an azeotrope with an immiscibility gap at a temperature ranging from 20 °C to 110 °C under normal pressure.

The term "under normal pressure" is to be understood in the specification and in the claims to mean atmospheric pressure (approximately 1 or about 10^5 Pa).

While at this point no theoretical interpretation has been arrived at for the invention, it has been found that azeotropic preparations which may be used as an active cleaning liquid in the process claimed for the invention are clear at low temperatures ranging, for example, from 20 to 25 °C. In other words, the components are fully dissolved in each other. Specific component composition relationships are established at each temperature in

the mixed phase. The phases which are separated at high temperatures can be converted to an emulsion milky in appearance by means of suitable process steps, such as preferably treatment with ultrasound, intensive movement during transfer by pumping or agitation, etc. This emulsion exhibits continuous droplets of the organic component(s) in a continuous aqueous phase. The emulsion possesses an excellent fat dissolving capability on the basis of its content of organic components (with molecules having lipophilic groups), but on the basis of the continuous aqueous phase also dissolves water-soluble, e.g., ionic, fouling substances such as salts. When the temperature of an azeotropic preparation is raised further the preparation passes into the vapor phase, in which the components are present in the specific composition typical of the particular azeotrope. During condensation the azeotropic preparation again migrates through the immiscibility gap; consequently, condensing vapor of the azeotropic preparation is present again on the articles to be cleaned, in the form of the emulsion, which possesses excellent dissolving properties both for lipid and for ionic fouling substances.

In the light of the criteria indicated above some organic components which form homogeneous azeotropes with water are given preference for use as organic components in azeotropic preparations employed for application of the process claimed for this invention. As may readily be discerned by experts in this area of the art, the invention is nevertheless not limited to the preferred compounds forming azeotropes.

The preferred compounds can best be described by the following general formula



where

- R^1 and R^3 each represent independently of each other; straight-chain or branched unsaturated C_1 - to C_{18} - alkyl groups in which one or more nonadjacent $-CH_2-$ groups may be replaced by $-O-$; saturated or unsaturated cyclic C_1 - to C_8 - alkyl groups in which one or more nonadjacent $-CH_2-$ groups may be replaced by $-O-$; hydroxy; C_1 - to C_8 - alkoxy; amino, where one or both hydrogen group(s) may be replaced by C_1 - to C_8 - alkyl groups; and

- X represents $-O-$, $-C(=O)-$; $-C(=O)-O-$; NH ; $-NR^1-$; $-N(-OH)-$; straight-chain or branched $-(C_1$ - to $C_8-)$ alkylene groups in which one or more nonadjacent $-CH_2-$ groups may be replaced by $-O-$; and n represents integers 1, 2, 3, etc.

In other words, the organic components of the azeotropic preparations which may be used in the process claimed for this invention may be selected from among organic compounds belonging to the groups of alcohols, glycols, amines, ethers, glycol ethers, esters, ketones, and amino alcohols and from among N-heterocyclene or organic acids.

In an especially preferred procedure compounds of the general formula indicated above are used as an organic component or components of the azeotropic preparation or as an additional organic component or components in which R^1 and R^3 each independently represents saturated C_1 to C_{12} alkyl groups, and with even greater preference saturated or unsaturated C_1 - to C_8 - alkyl groups in which one or more nonadjacent CH_2 group(s) may be replaced by $-O-$; may represent hydroxy, C_1 - to C_8 - alkoxy and unsubstituted or alkyl group substituted amino groups; and/or X represents $-O-$; $-C(=O)-$; $-C(=O)-O-$; $-NH-$; $-NR^1-$; $-N(-OH)-$; $-OCH(R^2)-CH_2-$ (where R_2 represents H or methyl); and n represents 1 or 2).

Specific examples of groups represented by R^1 and R^3 are hydrogen, methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl, i-

butyl, tert-butyl, n-pentyl, n-hexyl, n-octyl, furfuryl-2, tetrahydrofurfuryl-2, hydroxy, methoxy, thoxy, and propoxy. Specific examples of the groups represented by x are -O-; -C(=O); -C(=O)-O-; -NH-; -NR¹-; -N(-OH)-; ethyleneoxy; and propyleneoxy.

Even more preferred processes as claimed for the invention employ compounds of the general formula indicated above as an organic compound or compounds of the azeotropic preparations or as an additional organic component or components which are selected from among those in the group

- (C₁- to C₁₂-Alkyl) - C(=O)-O - (C₁- to C₁₂-Alkyl);
- (C₁- to C₁₂-Alkyl) - O - (C₁- to C₁₂-Alkyl);
- (C₁- to C₁₂-Alkyl) - C(=O) - (C₁- to C₁₂-Alkyl);
- (C₁- to C₁₂-Alkyl) - [N - (H or C₁- to C₁₂-Alkyl) (H or C₁- to C₁₂-Alkyl)];
- HO-(CH₂)_{1, 2, ... etc.} - [NH₂ or NH(C₁- to C₁₂-Alkyl) or N(C₁- to C₁₂-Alkyl)₂];
- H - [O - CH(H or CH₃) - CH₂]_{1, 2, ... etc.} - OH; and
- (H or C₁- to C₁₂-Alkyl) - [O - CH(H or CH₃) - CH₂]_{1, 2, ... etc.} - [OH or O(C₁- to C₁₂-Alkyl)].

Specific examples of organic components which may be used, either singly or together in groups of a plurality of the compounds named in azeotropic preparations of the active cleaning liquid, are selected from the group comprising propyleneglycol ether; dipropyleneglycol mono-n-propylether; tripropyleneglycol monomethylether; 3-methoxy-3-methylbutanol; furfuryl alcohol; tetrahydrofurfuryl alcohol; 1-aminobutanol-2; monoisopropanolamine; 2-amino-2-methylpropanol-1; 2-amino-2-methylpropanediol-1,3; 3-(aminomethyl)pyridine; ethanolamine; furfurylamine; methyl lactate; isopropyl lactate;

aminoacetaldehyde dimethylacetal; 4-aminomorpholine; 1-methylimidazole; 1,2-dimethylimidazole; 1-vinylimidazole; 1,4-diazabicyclo[2.2.2]octane (DABCO); 1,5-diazabicyclo[4.3.0]non-5-ene; and 1,8-diazabicyclo[5.4.0]undec-7-ene.

Addition to the active cleaning liquid for the process claimed for the invention of at least one cleaning booster which does not spontaneously evaporate corresponds to another especially preferred embodiment. It or they should preferably be distilled with the azeotropic preparation. Such cleaning boosters which do not spontaneously evaporate are known to the expert from the state of the art and require no further specification at this point.

It is also claimed for the invention that it is preferable to add at least one corrosion proofing additive to the active cleaning liquid. Such additive or additives should preferably be distilled with the azeotropic preparation. Such corrosion proofing additives are particularly advantageous when articles of nonferrous heavy metals or light metals are to be cleaned. For example, excellent cleaning of aluminum articles can be accomplished with an azeotropic preparation comprising 1-methylimidazole, which acts as an inhibitor. Copper parts may also be cleaned to advantage with azeotropic preparations comprising 1-methylimidazole. Brightening of the surface is achieved in the process. In place of the compound indicated, use may also be made of other corrosion proofing additives and inhibitors known to the expert from the state of the art.

Especially to be preferred, as yielding excellent cleaning results, are processes for cleaning articles as claimed for the invention in which an azeotropic preparation of water and an organic component is added as active cleaning liquid. By preference the organic component is in this instance a compound selected from among those in the group comprising dipropylene glycol monomethyl ether; dipropyleneglycol mono-n-

propyl ther; tripropylen glycol m nomethylether; 3-methoxy-3-methylbutanol; furfuryl alcoh 1; tetrahydrofurfuryl alc h 1; 1-aminobutanol-2; furfuryl amin ; methyl lactat and isopropyl lactate.

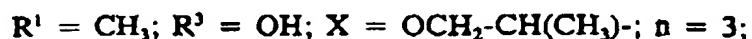
The compounds indicated belong to the following groups of compounds of the general formula $R^1 - [X]_n - R^3$.

(A) Glycol ethers:

- organic component No. 1: dipropyleneglycolmonomethylether



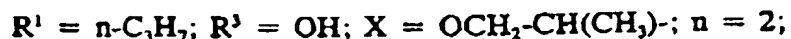
- organic component No. 2: tripropyleneglycolmonomethylether



- organic component No. 3: 3-methoxy-3-methylbutanol

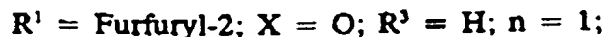


- organic component No. 4: dipropyleneglycol-n-propylether

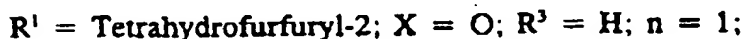


(B) Alcohols:

- organic component No. 5: furfuryl alcohol



- organic component No. 5: tetrahydrofurfuryl alcohol



(C) Amines:

- organic component No. 7: 1-aminobutanol-2



- organic component No. 8: furfurylamin

$R^1 = \text{Furfuryl-2}; X = -\text{NH-}; R^3 = \text{H}; n = 1;$

- organic component No. 11: 2-amino-2-methylpropanol-1

$R^1 = \text{CH}_3; X = \text{CH}_3 - \text{C} - \text{CH}_2\text{OH}; R^3 = -\text{NH}_2; n = 1;$

- organic component No. 12: 2-amino-2-methylpropanediol-1,3

$R^1 = \text{HOCH}_2; X = \text{CH}_3 - \text{C} - \text{CH}_2\text{OH}; R^3 = -\text{NH}_2; n = 1;$

(D) Esters:

- organic component No. 9: methyl lactate

$R^1 = \text{Hydroxyethyl}; X = \text{C}(=\text{O})\text{O-}; R^3 = \text{CH}_3; n = 1;$

- organic component No. 10: isopropyl lactate

$R^1 = \text{Hydroxyethyl}; X = \text{C}(=\text{O})\text{O-}; R^3 = i\text{-C}_3\text{H}_7; n = 1;$

In azeotropic preparations of this kind to be used as an active cleaning liquid in the process claimed for the invention, water and an organic component are to be added in relative amounts of $(100 - x)$ percent by weight: x percent by weight. In this statement x ranges from 0 ($x \leq 35$, is preferably in the range $3 \leq x \leq 25$, and by special preference in the range $4 \leq x \leq 15$).

In another preferred process the mixture ratio of water to the other component(s) in the azeotropic preparation is set more or less at the ratio which is present in the vapor as a result of heating of the liquid azeotropic preparation.

In another, also preferred, embodiment the process claimed for the invention for cleaning articles includes a step in which an azeotropic preparation of water and two organic components is used as the active cleaning liquid. By particular preference use is made of the active cleaning liquid of an azeotropic preparation consisting of water, dipropyl leglycolmono-n-propyl th r and an additional organic comp n nt. Th azeotropic preparation mploy d

as active cleaning liquid may, of course, also contain other components, such as at least one cleaning booster which does not spontaneously evaporate and by special preference is distilled with the azeotropic preparation, a cleaning booster such as is known from the state of the art and has been referred to in the foregoing, and/or at least one corrosion proofing additive or corrosion proofing inhibitor (by special preference one distilled with the azeotropic preparation) such as is also known as such or is known from the state of the art and has already been referred to in the foregoing.

In accordance with this preferred embodiment, by special preference use is made as an additional organic component of a compound in the group 1-aminobutanol-2; monoisopropanolamine; 2-amino-2-methylpropanol-1; 2-amino-2-methylpropanediol-1,3; 3-(aminomethyl-) pyridine; ethanolamine; aminoacetaldehydedimethylacetal; 4-aminomorpholine; 1-methylimidazole; 1,2-dimethylimidazole; 1-vinylimidazole; 1,4-diazabicyclo[2.2.2]octane DABCO; 1,5-diazabicyclo[4.3.0]non-5-ene; and 1,8-diazabicyclo[5.4.0]undec-7-ene.

The organic compounds indicated may be used singly or in combination with each other.

Also to be given particular preference is use of an additional organic component of the group made up of acetic acid, hydroxyacetic acid, formic acid, and butyric acid. The acids in question may also be used individually or in combination with each other or with other substances, such as the organic components named above.

In accordance with the preferred embodiment just described use is made as active cleaning liquid of an azeotropic preparation consisting of water, a glycolether (preferably dipropylene glycol monon-propylether) and an additional organic component in relative amounts of 90 percent by weight : (10 - y)

percent by weight : y percent by weight, where y is in the range $0 < y \leq 5$, and by special preference $0 < y \leq 2$.

A schematic drawing is presented in the attached drawing of a device in which the process claimed for the invention may be applied: a storage tank 2 with a separation compartment 4 and an overflow compartment 6 is connected by way of a feed pump 8 and a heating device 10 to a cleaning device 12. The interior of the cleaning device, whose structure is of the state of the art and which may include cleaning nozzles, a revolving basket, etc, is in the example shown in the figure is connected to a pressure compensation vessel 14, which, however, is not essential for operation.

Piping leads from the bottom of the cleaning device 12 to a filter device 16. The filter device 16 is connected by way of piping to a feed pump 18 on the top of the separation compartment 4. Additional piping extends from the filter device 16 by way of a vacuum pump 20 through a condenser 22 and a cooler 24 back to the separation compartment 4.

Piping also extends from the overflow compartment 6 by way of a delivery pump 26 through a heat exchanger 28 into a distillation device 30 and thence back into the cleaning device 12 or back to the storage tank 2.

A feed line 32 charging the storage tank 2 with active cleaning liquid extends into the storage tank 2. The storage tank 2 also contains a device, not shown, for removal of sludge deposited in the separation compartment 4.

Ventilation piping 34 extends into the normally sealed cleaning device 12.

The structure of the individual structural elements of the cleaning device 12 and an electric control unit (not shown) for the individual structural components is of the state of the art and is consequently not described in detail.

The device described operates as follows. After the cleaning device 12 has been charged with an article or articles to be cleaned, in an exemplary but not restrictive embodiment first liquid cleaning is carried out in which the feed pump 8 is actuated and active cleaning liquid, whose temperature may if desired be adjusted in the heating device 10, is fed to the cleaning device 12. In the cleaning device 12 the revolving article or articles to be cleaned is/are immersed and/or the article or articles to be cleaned are sprayed with liquid. The liquid is removed from the cleaning device 12 through the filter device 16 by the feed pump 18 and is fed into the separation compartment 4. Predominantly inorganic fouling substances are precipitated in the filter device 16 and are removed. Predominantly fatty fouling substances are precipitated in the separation compartment 4 and are also removed.

The liquid cleaning stage described as an example is followed by rinsing under the same conditions with active cleaning liquid from the tank 6.

The rinsing is followed by a steam cleaning or steam rinsing stage in which the feed pump 26 is actuated and then the active cleaning liquid is heated in the distillation device and converted to vapor. Because of the azeotropic nature of the azeotropic preparation employed as active cleaning liquid, this vapor has a predetermined content of water and the additional component or components. The composition of the liquid azeotropic preparation is preferably such that it corresponds in point of content to the components in the vapor phase. In the cleaning device 12 the vapor comes into vigorous contact with the article or articles to be

clean d; at least a part of th vapor is condens d. The fe d pump 18 d livers th condensat to th pr cipitation compartment after this cond nsat has passed through th filt r devic 16.

The liquid may be reconditioned if the vapor is fed back into th storage tank 6 from the distillation device 30 by way of the c ndenser 22 and the cooler 14.

The vapor cleaning or vapor rinsing is advantageously followed by circulating air drying or vacuum drying. In the process the vapor present in the cleaning device 12 is drawn off by the vacuum pump 20, the condensate formed in the cleaning device 12 passing through the filter device 16. The vapor mixed with the condensate is returned to the storage tank 2 as liquid after passing through the condenser 22 and cooler 24.

After vacuum drying has been completed, the separation compartment 4 is aerated by way of the aeration line 34, and the cl aned article(s) may be removed.

In an alternative embodiment, which also yields favorable r sults, articles to be treated are sprayed in the cleaning device 12 with the azeotropic preparation used as active cleaning liquid. In this process articles to be cleaned are soaked in the liquid. The subsequent process steps are more or less the same as those described in the foregoing.

After treatment the articles treated are in a distinctly better condition than after treatment in a conventional process, that is, by use of conventional organic solvents for the cleaning st ps under identical conditions. In particular it has been found, surprisingly, that all organic fouling substances, in particular inorganic salts from perspiration, coloring pigments, etc, are removed in addition to all organic fouling substances such as

lipophilic or oleaginous or fatty substances. The articles treated have no unpleasant odor and are outstanding in appearance.

As was stated earlier, azeotropic preparations with an immiscibility gap exhibit a surprisingly efficient cleaning behavior distinctly superior to that of conventional preparations.

Whenever use is made of azeotropic preparations with an immiscibility gap, in treatment in the liquid phase articles to be cleaned are brought into contact with an azeotropic preparation which is in a state such that the components of the azeotropic preparation are present in separate, or at least partly separate, phases. For example, liquid azeotropic preparations in a state of phase separation are treated with ultrasound or are vigorously transferred by pumping or agitated so that a milky emulsion of the azeotropic preparation is formed. This emulsion efficiently dissolves not only fatty or oily components but ionic or saline fouling substances as well.

Whenever articles to be cleaned are treated with the azeotropic preparation in the vapor phase, as described above the azeotropic preparation is heated and a vapor is produced in which the components are present in the quantitative proportions determined by the characteristic azeotropic properties. The vapor condenses at least to some extent on the articles to be cleaned, and the same milky emulsion is obtained as in the liquid phase. Efficient dissolving of fats and salts is observed in this instance as well.

When the temperature of the azeotropic preparation is raised to the point of liquid phase/vapor phase transition, the components pass into the vapor phase in the quantitative proportion corresponding to that of the azeotrope, and the azeotropic preparation can be produced by distillation without any problem.

The last-named embodiment of the process claimed for the invention is particularly favorable for the cleaning of metal parts. Thus, for example, lapping and polishing pastes can be very efficiently removed from metal parts by use of azeotropes with an immiscibility gap. For instance, an azeotropic preparation compounded with acid additives is used as active cleaning liquid for this purpose. Cleaning is carried out in the one-compartment system described above and may be conducted continuously or in a batch process.

SMD adhesives (SMD = surface mounted devices) such as are employed in manufacture of SMD components can also be removed surprisingly well from electronic components produced in double-sided assembly to prevent components from being detached during the soldering process. The adhesive is customarily applied by way of dispenser systems or templates before the printed circuit boards are secured. Defectively printed or dispensed circuit boards or templates may be cleaned. Surprisingly, cleaning results distinctly superior to those obtained with conventional solvents such as butyl acetate or isopropanol can be obtained with the azeotropic preparations used as claimed for the invention. In addition, precautionary measures (such as those taken to prevent explosions when correspondingly hazardous solvents are used) are superfluous.

The azeotropic preparations indicated may be used similarly by the process claimed for the invention to remove excess soldering paste applied during soldering simply and in an environmentally friendly manner from defectively printed circuit boards and templates. It is also possible to remove excess fluxing agent residues after soldering. Cleaning is accomplished by spraying, spray rinsing, and drying of articles to be cleaned, preferably in an immersion process involving ultrasound (cleaning stage), rinsing with or without ultrasound (rinsing stage), and drying. Cleaning is carried out preferably at a temperature in the range of 40-60

°C, but is not restricted to this temperature range. The temperature may be significantly higher, for example, it may even exceed 100 °C, especially in treatment of articles to be cleaned during the cleaning stage with the vapor of the azeotropic preparation.

Particular preference is given to use of the azeotropic preparation presented in Table I below for cleaning processes as claimed for the invention. Also given in this table are the preferred proportions of organic components (O.K.) to water, the boiling points of a particular azeotropic preparation, and the temperatures at which exemplary treatment of articles to be cleaned may be carried out. The invention is not, of course, restricted to the proportions of the components and treatment temperatures indicated.

In the event of use of azeotropes with an immiscibility gap particular preference is given to three-component mixtures of water, dipropyleneglycolmono-n-propylether, and amine compounds or n-heterocyclic compounds or organic acids, as shown in Table II below. An exemplary but not restrictive composition of the azeotropes is as follows: water (90 percent by weight), dipropyleneglycolmono-n-propylether (10 percent by weight), and y percent by weight of the compounds indicated in Table II.

Table I

Azeotropic Preparation		Boiling Point (°C)	Treatment Temperature (°C)
Organic Components (O.K.)	O.K. to Water Ratio		
No. 1	8.9 : 91.1	99.2	60
No. 2	7.9 : 92.1	99.1	60
No. 3	11 : 89	99 - 101	65
No. 4	10 : 90	100	65
No. 5	20 : 80	98.5	60
No. 6	10.5 : 89.5	102	65
No. 7	4.7 : 95.3	102	65
No. 8	30.9 : 69.1	100	60
No. 9	20 : 80	99.5	60
No. 10	34 : 76	98	60
No. 11	5 : 95	98	65
No. 12	6.5 : 93.5	101	60

Tabl II

Organic Components	γ (% by weight)	Boiling Point (°C)
1-Aminobutanol-2	0,3	101
Monoisopropanolamine	0,8	100
2-Amino-2-methyl-propanol-1	1,3	102
2-Amino-2-methyl-propandiol-1,3	1,5	101
3-(Aminomethyl-)pyridine	0,16	101
Ethanolamine	0,3	104
Aminoacetaldehyd-dimethylacetal	2,4 3,4 4,2	101
4-Aminomorpholine	0,4	101
1-Methylimidazole	0,1	101
1,2-Dimethylimidazole	0,1	100 - 102
1-Vinylimidazole	0,3	101
DABCO	0,03 0,08 0,1	101 - 103
1,5-Diazabicyclo-[4.3.0]non-5-en	0,02	100 - 103
1,8-Diazabicyclo-[5.4.0]undec-7-en	0,02	101 - 103
Acetic Acid (80 %ig)	1,5	100 - 101
Hydroxyacetic Acid	0,5	100 - 101
Formic Acid	1,5	100 - 101
Butyric Acid	1,2	100 - 101

The boiling point ($^{\circ}\text{C}$) of the azeotropic preparation made up of water, dipropyl neglycolmono-n-propylether, and the compounds indicated is also given in Table II.

The invention is illustrated by the following examples, but is not restricted to these examples.

Example 1

The drum of the cleaning device 12 described above was charged with material to be cleaned. The material, consisting of textiles, was in a first step treated under liquid cleaning conditions with azeotropic preparations at elevated temperatures. The azeotropic preparations and the pertinent treatment temperatures are indicated in Table I above. The material was dipped into the hot azeotropic preparation during agitation. The hot azeotropic preparation was fed in a closed loop from the drum of the cleaning device 12 through a filter device 16 and delivered to the separation compartment 4. In the filter device 16 predominantly inorganic fouling (salts) was deposited and also removed.

The first treatment step was followed by a second treatment step also carried out under liquid treatment conditions. Fresh azeotropic preparation (see Table I for the composition; in each preparation the azeotropic preparation of the second treatment step was of the same composition as that of the first step) was fed to the drum of the cleaning device at an elevated temperature. The material was delivered in a second closed loop from the drum of the cleaning device 12 to the separation compartment 4 by way of a filter device 16. The inorganic and organic substances were separated in the same way as in the first treatment step.

The second treatment step was followed by a third treatment step in which the material to be treated was treated with the vapor

of the particular azeotropic preparation, the composition of which was that typical of the particular azeotropic preparation (see Table I). After passing through the feed pump, the azeotropic preparation was converted to the vapor phase in a distillation device. The vapor was brought into intimate contact with the material to be treated in the drum of the cleaning device 12. Part of the vapor was condensed at the time of contact with the material. The liquid from the cleaning step following condensation was removed from the drum and, after passing through the filter device 16 for separation of the organic substances, was delivered to the separation compartment 4, where organic contaminants were separated. The vapor not already condensed in the drum of the cleaning device 12 was withdrawn from the drum, condensed, and (after optional filtration) delivered to the storage tank 2 for future use.

After the vapor of the azeotropic preparation had been removed, the drum was evacuated, for example at 10^{-2} bar, and the remaining vapor was removed in the same way as described above. The hot treated material released the water and the organic components of the azeotropic preparation in the vacuum, with the result that the material was dry after 10 minutes of vacuum treatment.

The material to be treated was in much better condition than such material treated by conventional means. Both inorganic and organic fouling substances were removed in their entirety. The material gave off no unpleasant odor and was outstanding in appearance. It was successfully ironed or pressed.

The third step (vapor treatment) is not absolutely necessary after liquid cleaning; results just as good as those described above can also be obtained with no vapor treatment. It is claimed for the invention that it is also possible to replace the steps of

tr at m nt of material to b tr at d, in whol or in part, by steps of treatment with az otropic pr paration in vapor form. Equally good cl aning results wer obtain d with this proc dure as w ll.

Example 2

Defectively printed circuit boards or templates produced in SMD manufacture were treated with a three-component mixture of water, dipropyleneglycolmono-n-propylether or an amine compound or N-heterocyclic compound or organic acids, such as is shown by way of example in Table II. The three-component mixtures used as active cleaning liquids consisted of 90 percent by weight water, 10 - y percent by weight dipropyleneglycolmono-n-propylether, and y p rcent by weight of one of the compounds listed in Table II. Cleaning was accomplished by the spray process.

In order to remove SMD adhesives, the circuit boards or templates were treated at the temperatures indicated in Table II with liquid azeotropic preparations, the treatment being accompanied by application of ultrasound (ultrasound is not, h wever, absolutely necessary for obtaining good cleaning results). The azeotropic preparations were in the form of a milky emulsion which became almost clear when ultrasound was applied. All traces of the adhesives were removed, without the need for providing protective devices in the system, such as ones protecting against xplosion.

The cleaning results were considerably better than those obtained by application of conventional solvents such as butyl ac tate or isopropanol. In addition, in the case of the latter two it is absolutely necessary to provide protection against explosion for labor safety reasons.